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(19) THE PATENT OFFICE LONDON

(54) METHOD OF PRODUCING A POLYETHYLENE-2,6-NAPHTHALATE YARN

(71) We, TEIJIN LIMITED, a Japanese body corporate, of No. 1 Umeda Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of drawing undrawn filaments of a naphthalate polyester, and in particular, to a method of producing commercially with good process operability a naphthalate polyester yarn of good mechanical and thermal properties.

An attempt to produce a naphthalate polyester yarn of good mechanical and thermal properties by subjecting to multistage drawing by the pin-plate method an undrawn yarn of polyethylene - 2,6 - naphthalate containing at least 95 mol % of ethylene-2,6-naphthalate units and of an intrinsic viscosity of at least 0.5 has been made in the past. For instance, in U.S. Patent 3,616,832 there is disclosed that a polyethylene - 2,6 - naphthalate yarn of high tenacity, high Young's modulus and good thermal resistance is produced by drawing such an undrawn yarn in two or three stages by the pin-plate method.

However, in this method it was difficult to fix the drawing point and the uniformity of the drawing was poor, with the consequence that wrapping of the yarn and yarn unevenness tended to occur during the drawing operation. Further, there was the shortcoming that owing to the friction between the yarn and the pin and plate, it was difficult to achieve a high drawing speed and, as a result, the productivity was low. These drawbacks were especially marked when drawing yarns of heavy denier composed of a great number of filaments, which are used as industrial materials.

It is therefore an object of the present invention to provide a method which can produce a yarn of good mechanical and thermal properties, especially a high denier yarn, in which the yarn can be drawn at high speed and with good drawing stability.

We have found that this object can be achieved by drawing the filaments in two or more stages under very specific conditions.

More particularly, the invention consists in a process for drawing undrawn filaments composed of an ethylene - 2,6 - naphthalate polymer (as hereinafter defined) having an intrinsic viscosity (measured as hereinafter described) of at least 0.45, which process comprises:

(a) drawing the filaments in a first stage between feed rollers at 110—150° C. and first stage draw rollers at 170—220° C., the draw ratio being at least 5.0 and 85—95% of the total draw ratio, and
(b) drawing the filaments from step (a) in a second stage between the first stage draw rollers and second stage draw rollers at a temperature of 190—250° C. which is at least 10° C. higher than the temperature of the first stage draw rollers.

step (b) being followed by further drawing if desired, or if necessary to give a total draw ratio of at least 5.5.

The term "polyethylene - 2,6 - naphthalate" or "ethylene - 2,6 - naphthalate polymer" as used herein means a polyester containing units derived from naphthalene - 2,6-dicarboxylic acid, units derived from ethylene glycol and optionally units derived from one or more dicarboxylic acids other than naphthalene - 2,6 - dicarboxylic acid and/or dihydric alcohols other than ethylene glycol, the sum of the molar percents of said other dicarboxylic acids (based on the total dicarboxylic acid compound) and said other dihydric alcohols (based on the total dihydric alcohol component) being not more than 5 mol %.

While polyethylene - 2,6 - naphthalate homopolymer is typical of this type of polyester, the polyester may, for example, be a copolymer containing a suitable third component. Such third component may be a compound having two ester-forming functional groups, for example an aliphatic dicarboxylic acid such as oxalic, succinic, adipic or sebacic acid; an alicyclic dicarboxylic acid such as

cyclopropanedicarboxylic, cyclobutanedicarboxylic or hexahydroterephthalic acid; an aromatic dicarboxylic acid such as orthophthalic, isophthalic, terephthalic, naphthalene - 2,7 - dicarboxylic or diphenyldicarboxylic acid; an acid containing ether groups such as diphenyletherdicarboxylic or diphenoxydiethanedicarboxylic acid; a dicarboxy-aromatic sulphonate such as sodium - 3,5 - dicarboxybenzenesulphonate; or a hydroxycarboxylic acid such as glycollic, *p*-hydroxybenzoic or *p*-hydroxyethoxybenzoic acid. Or it may be a dihydroxy compound, or a functional derivative thereof such as propyl glycol, trimethylene glycol, diethylene glycol, tetramethylene glycol, hexamethylene glycol, neopentylene glycol, *p*-xylene glycol, 1,4-cyclohexanedimethanol, bisphenol A, p,p' - diphenoxysulphone, 1,4-bis(beta - hydroxyethoxy)benzene, 2,2 - bis-(*p* - beta - hydroxyethoxyphenol)propane, a polyalkylene glycol or *p* - phenylenebis-(dimethylsiloxane). Or it may be a polymer derived from one or more of the foregoing carboxylic acids, hydroxycarboxylic acids, dihydroxy compounds, and functional derivatives thereof. The third component may also be a compound having only one ester-forming functional group, such as benzoic acid or a monomethyl ether of a polyalkylene glycol; or it may have three or more ester-forming functional groups, for example glycerol, pentaerythritol or trimethylol propane, so long as the polyester obtained is substantially linear. The polyester may contain a delustrant such as titanium dioxide and/or a stabilizer such as phosphoric or phosphorous acid or an ester thereof.

The intrinsic viscosity of the polymer is as measured in a 6:4 solvent mixture of phenol and orthodichlorobenzene at 35° C.; it must be at least 0.45, and preferably 0.55 to 1.0. The birefringence of the undrawn filaments will in practice be within the range 0.001—0.01. The invention is of special advantage when applied to filaments of total denier 3000—14,000.

The undrawn filaments can be made using a melt-spinning apparatus having a spinning cell below the spinneret, such as is conventionally used in processes for spinning linear polyesters of high degree of polymerisation in which the temperature of the atmosphere surrounding the spun filaments below the spinneret is gradually decreased proportionally to the distance travelled from the spinneret. In the present process this temperature (T°C.) is preferably so controlled over the whole zone extending from the point immediately below the spinneret to the point where it equals the second order transition point of the polymer, that it is always within a range that satisfies the following relationships with the spinning temperature (Ts°C.) and the distance from the spinneret (Xcm).

(1) when $0 < X \leqq X_1$
$2X - 10 \leqq T - Ts \leqq 6X + 10$

(2) when $X_1 < X \leqq X_2$
$2X_1 - 10 \leqq T - Ts \leqq 6X_1 + 10$

(3) when $X > X_2$
$2X_1 - 6.4(X - X_2) - 10 \leqq T - Ts \leqq 6X_1 - 3.8(X - X_2) + 10$

where X is the distance from the spinneret, $X_1 = 7Q$ and $X_2 = 22Q$ (cm).

where Q is the flow rate through a spinneret orifice (g/min).

If the temperature of the atmosphere surrounding the spun filaments is decreased proportionally to the distance from the spinneret, the degree of molecular orientation of the product is slightly lower than in the complete absence of control, but it may still be too high to allow subsequent drawing to a sufficiently high draw ratio for the present purposes. On the other hand, the filaments obtained when the temperature of the atmosphere is controlled as described above has the following advantages: a) The degree of polymerisation falls only slightly during the spinning; b) the degree of molecular orientation is sufficiently low for drawing to be carried out to a high degree; c) the denier and orientation are very uniform; and d) the drawability is good. Such filaments can thus be drawn to a higher draw ratio than in corresponding filaments spun by the conventional methods.

Figure 1 of the accompanying drawings illustrates the difference between (a) temperature control that satisfies the above relationships (1), (2) and (3) and (b) the conventional procedure in which the temperature is gradually decreased proportionately to the distance from the spinneret using a spinning temperature (Ts) of 315° C., and a flow rate through a spinneret orifice (Q) of 1.57 grams per minute. The crosshatched portion A indicates where the conditions that satisfy the said relationships are satisfied, whereas the crosshatched portion B indicates the conditions in the conventional method.

As is apparent from FIGURE 1, when the temperature of the atmosphere surrounding the spun filaments is so controlled as to satisfy the relationships (1), (2) and (3), the temperature in the neighborhood of the spinneret is close to the spinning temperature, and for a certain distance immediately below the spinneret it gradually rises; and thereafter for a further distance the temperature is maintained substantially constant, after which it gradually falls.

Methods of carrying out the invention will now be specifically described by reference to

Figures 2 and 3 of the accompanying drawings, which are schematic side views of two examples of suitable apparatus.

Referring to FIGURE 2, polyethylene-2,6-naphthalate undrawn filaments Y are conveyed via a pair of nip rollers 1a and 1b to a set of hot feed rollers 2a, 2b, 2c, 2d, 2e, 3a and 3b maintained at a temperature of 110—150° C., and preferably 120—140°C. between the nip rollers and the hot feed rollers, and the filaments are pre-stretched, after which they are heated by the hot feed rollers. This set of rollers may include also one or more unheated rollers, so long as the filaments leaving the last roller are adequately heated. In the embodiment shown in FIGURE 2, of the hot feed rollers, rollers 3a and 3b are of smaller diameter than the other rollers 2a, 2b, 2c, 2d and 2e being below 70 millimeters in diameter. While the use of these rollers with smaller diameter is to be preferred, it is not necessary. To ensure that the filaments are thoroughly preheated, they are preferably in contact with the several hot rollers for a total time of at least 1.1 seconds. Further to facilitate fixation of the drawing point, it is best to cause the filaments to make contact with the final roller 3b with a wrapping angle of at least 180°.

The heated filaments Y, are then conveyed to a set of first stage draw rollers 4a, 4b, 4c, 4d and 4e which are at a temperature of 170—220° C., preferably 180—210° C. by means of which they are drawn at least 5.0x, and preferably at least 5.5x. The draw ratio at this stage must be 85—95% of the total draw ratio. To ensure that sufficient heat is imparted to the filaments it is preferred that the total time for which the filaments are in contact with the several hot first stage draw rollers is at least 0.3 second.

It has been found that a high draw ratio is more easily obtained if a jet of superheated steam is applied to the filaments at some point between the hot feed rollers and the first stage draw rollers, and it is therefore preferred that this should be done. From the first stage draw rollers the filaments are passed to a set of second stage draw rollers 6a, 6b, 6c, 6d, and 6e, which are maintained at a temperature of 190—250° C., preferably 200—230° C., and at least 10° C. higher than that of the set of first stage draw rollers, where the filaments are both further heated and further drawn (between the first and second stage draw rollers) to a total draw ratio of at least 5.5x and preferably 6.0x. The filaments are preferably caused to contact the several hot second stage draw rollers for a total time of at least 0.24 second. One or more further stages of stretching may follow, and are indeed necessary if the total draw ratio at the end of the second stage is still below 5.5x.

Additional heat may be imparted to the filaments by the provision of a hot plate 5, preferably at 190°—250° C., between the first stage and second stage draw rollers. Other known heating means may be substituted for the hot plate 5.

The filaments which have been heated and drawn to the prescribed total draw ratio, are treated with a finishing agent by means of a finishing roller 7, and is then cooled by a means of a set of cooling rollers 8a, 8b, 8c and 8d and thereafter wound up.

In the method of operating illustrated by FIGURE 3, the hot feed rollers consist of a single pair of rollers 12a and 12b, the first stage draw rollers consist of a pair of rollers 13a and 13b, the second stage draw rollers consist of a pair of rollers 15a and 15b, nip rollers 11a and 11b correspond to the nip rollers 1a and 1b of FIGURE 2, and a slit heater 14 has been substituted for the hot plate 5 of FIGURE 2.

This method is particularly suitable when the filaments are to be heated and drawn in accordance with the invention immediately after being spun.

Unless all the specified conditions with respect to temperature and the draw ratios are satisfied, it becomes impossible to carry out the process at high speed as well as stably, nor can a polyethylene-2,6-naphthalate yarn of high denier and good mechanical and thermal properties be obtained. For instance, if the draw ratio of the first stage drawing is less than 85% of the total draw ratio and below 5x, the filaments undergo the second stage drawing while their structure is still unstable, with the consequence that the draw ratio obtainable in the subsequent stage or stages is insufficient.

On the other hand, if the first stage draw ratio exceeds 95% of the total ratio the drawability of the filaments at the second stage drawing is poor. Further, if the temperature of the hot feed rollers is below 110° C. it is impossible to meet the conditions specified for the first-stage drawing as regards draw ratio, and also the total draw ratio obtainable is too low; on the other hand, if the temperature of these rollers is above 150° C., not only does practically all of the first stage drawing tend to occur at these rollers, but also slippage rather than orientation of the molecules tends to take place during the drawing. Moreover, crystallisation of the filaments takes place concurrently with drawing and this causes difficulty in carrying out the subsequent drawing. Again, when the surface temperature of the feed rollers is too high, the fixation of the drawing point at these rollers becomes unstable, with the consequence that the association between the individual filaments becomes unsatisfactory and the uniformity of the drawing suffers, so that when the yarn is subsequently heated, either yarn breakage or wrapping of the yarn

around the rollers takes place, impairing the drawing efficiency. On the other hand, if the temperature of the first stage draw rollers is below 170° C., the total draw ratio obtainable is too low and, in addition, it becomes difficult to achieve the necessary draw ratio in the first stage drawing, while if this temperature is above 220° C., considerable crystallisation of the filaments occurs at these rollers, making it difficult to carry out the second stage or subsequent drawings, and also the yarn tends to wrap around these rollers, reducing the drawing efficiency.

While the heated filaments have been given an effective molecular orientation by the first stage drawing, the heating in the second stage drawing step, if it complies with the specified conditions, not only promotes crystallisation among the highly orientated molecular chains, but also stabilizes the internal structure of the filaments without relaxing the orientation, increases the tenacity and Young's modulus, raises the melting point and improves the dimensional stability.

The drawing tension in the second stage drawing is preferably about equal to that in the first stage drawing and drawing is exceptionally satisfactory when the conditions employed are such that the respective tensions are about the same.

Naphthalate polyester yarns obtained by the process of the invention possess, in addition to the properties possessed intrinsically by naphthalate polyesters, the following advantages:

(a) High tensile strength, generally at least 8.5 g/d, and high toughness, generally at least 22.0 g $\sqrt{\%}$/de.

(b) High Young's modulus, at least 2500 kg/mm².

(c) Good dimensional stability to heat, the shrinkage under dry heat at 180° C. being not more than 7%.

(d) High melting point, the free-length melting point being at least about 279° C. and the constant-length melting point being at least 284° C. (The melting point is taken as the temperature at which an endothermic peak appears in the Differential Scanning Calorimeter curve determined for 8 mg of the sample at a heating rate of 10°C./min. using a Perkin-Elmer testing apparatus of the DSC 1 type).

(e) Very uniform quality with very little fuzz and unevenness of denier.

Yarns obtained by the method of the invention can be used for various purposes where tensile strength, toughness, resistance to tensile deformation or thermal resistance is required, and are especially valuable as a reinforcing material in such products as tyres, belts and hoses, where dimensional stability is important.

The following Examples illustrate the invention further. The mechanical and thermal properties given in the Examples were measured as follows:

Tenacity and Elongation

The yarn is conditioned for one day at a relative humidity of 65% at 25° C. A 20 cm sample is measured on an "Instron" (Registered Trade Mark) Tensile Tester at an extension rate of 100% per minute. The tenacity is calculated by dividing the tension at break by the denier of the unextended sample, and the elongation is the observed elongation at break.

Young's Modulus

The yarn is conditioned as before. A 20 cm sample is measured on an "Instron" Tensile Tester at an extension rate of 20% per minute. The Young's modulus is calculated from the ratio of stress to strain within the straight line part of the load-elongation curve up to 1% elongation.

Yarn Unevenness (U %)

The determination is made by the half-innert test, using the Uster yarn unevenness tester Type C manufactured by Zellweger Company, Switzerland, and the U % is obtained with an integrator.

Shrinkage

Shrinkage in boiling water is measured in the following manner. A five turn portion of sample is taken, using a sizing reel having a circumference of 1.125 meters. After removing the sample from the reel, the hank length (l) is measured under an initial load equal (in grams) to 1/30 the denier. This sample is then immersed in boiling water for 30 minutes, after which it is withdrawn and air-dried. The same load as before is applied and the hank length (l_1) is measured.

Shrinking at 180° C. dry heat is measured by determining l as before, suspending the sample in a dryer at 180° C. for 15 minutes and after it has cooled measuring the hank length (l_1) under the same load as before. In both cases the shrinkage is calculated as follows:

$$\text{Shrinkage} = \frac{1-l_1}{1} \times 100\ (\%)$$

Melting Point

Free-length melting point, is determined from the DSC curve obtained from measurements made on 8.5 mg of the sample at a heating rate of 10° C. per minute, using the Perkin Elmer DSC—I measuring instrument, and is the temperature at which the endothermic peak appears.

Constant length melting point (Tm) is defined as the peak temperature obtained under the following conditions. 7 mg of the

specimen is fixed to a stainless steel frame weighing 60 mg to maintain its length constant. The frame is then put into an aluminium pan together with 40 mg of silver powder. The measurement is made by means of a Perkin Elmer DSC—I type measuring instrument while heating at the rate of 10° C. per minute.

Example 1.

Polyethylene - 2,6 - naphthalate of $[\eta]=0.64$ (second transition temperature Tg= 113° C.) was melt-spun, and a spun yarn of 6800 denier/192 filaments was obtained. The spinning temperature (spinneret temperature) was 315° C., the spinneret had 192 holes, the flow rate was 302 grams per minute, and the spinning speed was 400 meters per minute. Three cylindrical heating tubes having lengths of 10, 20 and 30 centimeters were provided below the spinneret, and the temperature of the atmosphere surrounding the spun yarn was controlled so as to come within the range indicated by the hatched portion A of FIGURE 1. The yarn obtained in this manner has the properties shown in Table 1.

TABLE 1

$[\eta]_F$	Breaking strength	Elongation at break	Denier unevenness (U %)	Birefringence ratio $\Delta n \times 10^{-5}$
0.58	0.90 g/de	535 %	1.20 %	306

The two-stage drawing and heat treatment of this undrawn yarn was then carried out using the drawing apparatus shown in FIGURE 2. Except that the temperature of the hot feed rollers was varied as indicated in Table 2, the conditions were kept constant as indicated below, and the drawn yarn was wound up at a speed of 150 meters per minute.

Prestretch ratio: 1.007
Roller diameter (first five hot feed rollers, 1st stage draw rollers, 2nd stage draw rollers): 200 mm
Roller diameter of last two hot feed rollers: 45 mm
Preheating time: 3.34 seconds
Wrapping angle at last hot feed roller: 210°
First stage draw ratio: 6.02
Second stage draw ratio: 1.113
Ratio of first stage to total draw ratio: 89.8%
Total draw ratio: 6.70
First stage draw roller temperature: 190° C.
Total time of contact with first stage draw rollers: 0.91 seconds
Plate temperature: 210° C.
Second stage draw roller temperature: 210° C.
Total time of contact with second stage draw rollers: 0.73 seconds

The temperature of the hot feed rollers, the drawing efficiency, and the properties of the yarns obtained are shown in Table 2.

TABLE 2

Run No.		1	2	3	4	5	6	7
Temperature of hot feed rollers	°C	100	110	120	130	140	150	160
Drawing condition efficiency		good	good	good	good	good	good	poor
Tenacity	g/de	8.41	8.76	9.05	9.12	8.93	8.84	8.36
Elongation	%	5.6	6.6	7.0	7.6	8.0	8.2	6.2
Toughness	$g\sqrt{\%}/de$	19.9	22.5	24.0	25.2	25.3	25.3	20.8
Young's modulus	kg/mm^2	2410	2880	2950	3010	2970	2950	2340
Yarn unevenness (U %)	%	1.30	0.61	0.57	0.48	0.54	0.58	1.95
Shrinkage at boiling water	%	2.1	1.5	1.3	1.1	1.0	0.9	0.8
Free length m.p.	°C	268.2	278.6	279.1	280.6	280.3	280.1	267.5

(Toughness is expressed as $T\sqrt{E}$, where T is the tenacity in gpd and E is the percentage elongation.)

(Runs 1 and 7 are controls).

Example 2.

The undrawn yarn of Example 1 was given a two-stage drawing and heat treatment exactly as in Example 1, except that the temperature of the hot feed rollers was held constant at 130° C. and the temperature of the first stage draw rollers was varied. The first stage and second stage draw ratios and the change in the temperature of the first stage draw rollers were chosen so as to produce satisfactory drawing conditions in both stages. The ratio of the first stage draw and the properties of the yarn obtained are shown in Table 3.

The undrawn yarn of Example 1 was given a two-stage drawing and heat treatment exactly as in Example 1, except that the temperature of the hot feed rollers was held constant at 130° C. and the temperature of the first stage draw rollers was varied. The first stage and second stage draw ratios and the change in the temperature of the first stage draw rollers were chosen so as to produce satisfactory drawing conditions in both stages. The ratio of the first stage draw and the properties of the yarn obtained are shown in Table 3.

TABLE 3

Run No.		8	9	10	11	12	13	14	15
Temperature of 1st stage draw rollers	°C	160	170	180	190	200	210	220	230
1st stage draw ratio		4.81	5.52	5.86	6.02	6.10	6.14	6.16	6.18 (partial fusion)
2nd stage draw ratio		1.290	1.175	1.136	1.113	1.092	1.071	1.057	drawing not possible
Total draw ratio		6.20	6.49	6.65	6.70	6.66	6.56	6.51	–
Ratio of first stage of total draw ratio	%	77.6	85.2	88.1	89.8	91.5	93.4	94.6	–
Tenacity	g/de	8.34	8.76	8.96	9.12	9.03	8.83	8.69	–
Elongation	%	6.5	8.0	7.8	7.6	7.7	7.8	8.1	–
Toughness	$g\sqrt{\%}/de$	21.3	24.8	25.1	25.2	24.9	24.6	24.7	–
Young's modulus	kg/mm^2	2310	2850	2920	3010	3050	3070	2930	–
Yarn unevenness (U %)	%	0.46	0.44	0.45	0.48	0.51	0.55	0.61	–
Shrinkage at boiling water	%	3.8	1.8	1.3	1.1	0.9	0.8	0.6	–
Free length m.p.	°C	269.2	275.6	279.3	280.6	280.4	280.0	278.5	–

(Runs 8 and 15 are controls.)

Example 3.

The undrawn yarn of Example 1 was given the two stage drawing and heat treatment under the same conditions as in Example 1, except that the temperature of the hot feed rollers was held constant at 130° C. and the temperature of the second stage draw rollers was varied. The changes in the properties of the yarns obtained, resulting from the change in the temperature of the second stage draw rollers, are shown in Table 4.

TABLE 4

Run No.		16	17	18	19	20	21	22
Temperature of 2nd stage draw rollers	°C	185	200	210	220	230	240	260
Tenacity	g/de	8.47	8.82	9.12	8.93	8.74	8.61	
Elongation	%	5.8	7.1	7.6	7.7	7.9	8.2	Frequent breakage of yarn as a result of fusion of filaments at the 2nd stage draw rollers.
Toughness	$g\sqrt{\%}/de$	20.4	23.5	25.2	24.8	24.6	24.7	
Young's modulus	kg/mm^2	2450	2930	3010	3100	3150	3100	
Shrinkage at boiling water	%	2.0	1.5	1.1	0.9	0.7	0.5	
Shrinkage at 180°C. dry heat	%	7.5	6.2	5.5	4.8	4.5	3.8	
Free length m.p.	°C	272.1	278.7	280.6	281.2	280.5	280.3	

(Runs 16 and 22 are controls.)

m.p.	C	272.1	278.7	280.6	281.2	280.5	280.3	

(Runs 16 and 22 are controls.)

Example 4.

The undrawn yarn of Example 1 was given the two stage drawing and heat treatment as in Example 1, except that the temperature of the hot feed rollers was held at 130° C. and the plate interposed between the first and second stage rollers was removed. The properties of the resulting yarn are shown in Table 5 (Run 23).

TABLE 5

Run No.	Tenacity (g/de)	Elongation (%)	Toughness ($g\sqrt{\%}$/de)	Young's modulus (kg/mm²)	Shrinkage at boiling water (%)	Shrinkage at 180°C. dry heat (%)	Free length m.p. (°C)
23	8.72	6.4	22.1	2890	1.6	6.4	278.4
18	9.12	7.6	25.2	3010	1.1	5.5	280.6

(Run 18 is that in which the plate was not removed.)

Example 5.

The undrawn yarn of Example 1 given the two stage drawing and heat treatment under the same conditions as in Example 1, except that the temperature of the hot feed rollers was held at 130° C. and superheated steam at 300° C. was jetted against the yarn at a pressure of 0.15 kg/cm² gauge between the hot feed rollers and the first-stage draw rollers. In this experiment the first stage draw ratio, the total draw ratio and the ratio of the first stage to the total draw ratio are shown in Table 6 (Run 24) as are the properties of the resulting yarn.

TABLE 6

Run No.	1st stage draw ratio	Total draw ratio	Ratio of 1st stage to total drawing ratio (%)	Tenacity (g/de)	Elongation (%)	Toughness ($g\sqrt{\%}$/de)	Young's modulus (kg/mm²)	Yarn unevenness [U%] (%)	Shrinkage at boiling water (%)	Shrinkage at 180°C dry heat (%)	Fuel length m.p. (°C)
24	6.33	6.88	92.0	9.65	6.8	25.2	3200	0.51	1.3	5.8	281.3
18	6.02	7.70	89.8	9.12	7.6	25.2	3010	0.48	1.1	5.5	280.6

(In Run 18 superheated steam was not jetted against the yarn.)

$1.4 \times 10^{-3} / 1.20 \times 10^{4} \times D$

Example 6.

The undrawn yarn of Example 1 was given the two stage drawing and heat treatment as in Example 1 while holding the temperature of the hot feed rollers at 130° C., after which this drawn yarn was heated and given a third stage of drawing as a ratio of 1.046 by passing it over a plate heated to 215° C. and third stage draw rollers heated to 220° C. The properties of the three stage drawn and heat-treated yarn drawn to a total ratio of 7.0 are shown in Table 7 (Run 25).

TABLE 7

Run No.	Tenacity (g/de)	Elongation (%)	Toughness ($g\sqrt{\%}/de$)	Young's modulus (kg/mm^2)	Yarn unevenness [U%] (%)	Shrinkage at boiling water (%)	Shrinkage at 180°C. dry heat (%)	Free length m.p. (°C)
25	9.44	7.1	25.2	3130	0.46	1.5	6.3	281.5
18	9.12	7.6	25.2	3010	0.48	1.1	5.5	280.6

(In Run 18 yarn was drawn in two stages to a total ratio of 6.7.)

Example 7.

A yarn of polyethylene - 2,6 - naphthalate of $[\eta]=0.80$ was melt spun as in Example 1, and had the following properties: $[\eta]_F=0.70$, breaking strength=1.11 grams per denier, elongation at break=587%, denier unevenness (U%)=1.12% and

$$\Delta n=358 \times 10^{-5}.$$

This undrawn yarn was submitted to a two stage drawing and heat treatment under the same conditions as in Example 1, except that the yarn was preheated to 130° C. with the hot feed rollers, the first stage draw ratio was 5.19X, the total draw ratio was 6.5X, and the ratio of the first stage to the total draw ratio was 91%. The properties of the drawn and heat-treated yarn obtained are shown in Table 8.

TABLE 8

Run No.	Tenacity (g/de)	Elongation (%)	Toughness ($g\sqrt{\%}/de$)	Young's modulus (kg/mm^2)	Yarn unevenness [U%] (%)	Shrinkage at boiling water (%)	Free length m.p. (°C.)	Constant length m.p. (°C)
26	10.92	7.2	29.4	3340	0.57	2.0	280.5	285.7

265

Example [illegible] The conditions of the drawing and heat

Run No.	Tenacity (g/de)	Elongation (%)	Toughness ($g\sqrt{\%}/de$)	Young's modulus (kg/mm^2)	Yarn unevenness [U%] (%)	Shrinkage at boiling water (%)	Free length m.p. (°C.)	Constant length m.p. (°C)
26	10.92	7.2	29.4	3340	0.57	2.0	280.5	285.7

Example 8.

Polyethylene - 2,6 - naphthalate of $[\eta]=0.62$ was melt-extruded from a spinneret having 192 holes at a flow rate of 225 grams per minute and a spinning temperature (spinneret temperature) of 315° C. The temperature of the atmosphere surrounding the spun yarn was then controlled within the range shown by the hatched portion B of FIGURE 1 by the provision of a 30 centimeter long cylindrical heating tube below the spinneret. The spinning speed was 300 meters per minute. The resulting 6760 denier/192 filament undrawn yarn had the following properties: denier unevenness $(U\%)=1.5\%$, $[\eta]_P=0.56$, $n=350\times10^{-5}$. This undrawn yarn was immediately, without being wound up, given a two stage drawing and heat treatment using the apparatus shown in FIGURE 3, and the drawn yarn was wound up at 2000 meters per minute.

The conditions of the drawing and heat treatment were as follows:
Prestretch: 1.01
Diameter of rollers (hot feed, 1st stage draw and 2nd stage draw rollers): 180 mm
Temperature of hot feed rollers: 125° C.
Preheating time: 1.65 seconds
Wrapping angle at last hot feed roller: 230°
Temperature of 1st stage draw rollers: 195°C.
Contact time on 1st stage draw rollers: 0.33 seconds
Temperature of slit heater: 250° C.
Temperature of 2nd stage draw rollers: 215°C.
Contact time on 2nd stage draw rollers: 0.26 seconds
Draw ratio of 1st stage draw rollers: 6.21
Total draw ratio: 6.66
Ratio of the 1st stage to total draw ratio: 93.3%

The properties of the resulting drawn and heat-treated yarn are shown in Table 9.

TABLE 9

Run No.	Tenacity (g/de)	Elongation (%)	Toughness ($g\sqrt{\%}/de$)	Young's modulus (kg/mm^2)	Yarn unevenness [U%] (%)	Shrinkage at boiling water (%)	Shrinkage at 180°C. dry heat (%)	Free length m.p. (°C)	Constant length m.p. (°C)
27	8.82	6.8	23.0	2950	0.71	1.1	4.9	279.5	285.1

WHAT WE CLAIM IS:—

1. A process for drawing undrawn filaments composed of an ethylene - 2,6 - naphthalate polymer (as hereinbefore defined) having an intrinsic viscosity (measured as hereinbefore described) of at least 0.45, which process comprises

(a) drawing the filaments in a first stage between feed rollers at 110—150° C. and first stage draw rollers at 170—220° C., the draw ratio being at least 5.0 and 85—95% of the total draw ratio, and
(b) drawing the filaments from step (a) in a second stage between the first stage

draw rollers and second stage draw rollers at a temperature of 190—250° C. which is at least 10° C. higher than the temperature of the first stage draw rollers,

step (b) being followed by further drawing if desired, or if necessary, to give a total draw ratio of at least 5.5.

2. A process according to claim 1 wherein the total time that the filaments are in contact with the hot feed rollers in steps (a) and (b) is at least 1.1 seconds.

3. A process according to claim 1 or 2 wherein the total time that the filaments are in contact with the first stage draw rollers is at least 0.3 second.

4. A process according to claim 1, 2 or 3 wherein the total time that the filaments are in contact with the second stage draw rollers is at least 0.24 second.

5. A process according to any one of the preceding claims wherein the undrawn filaments have a birefringence of 0.001—0.010.

6. A process according to any one of the preceding claims wherein the filaments have a total denier of 3000 to 14,000.

7. A process according to any one of the preceding claims wherein the undrawn filaments are contacted with hot feed rollers consisting of a plurality of rollers, of which at least the final roller is of smaller diameter than the rest of the rollers, the diameter of said final roller being not greater than 70 millimeters and the wrapping angle of the filaments around said final roller being at least 180 degrees.

8. A process according to any one of the preceding claims which comprises prestretching the undrawn filaments before they are fed to the hot feed rollers.

9. A process according to any one of the preceding claims which comprises jetting superheated steam against the filaments between the hot feed rollers and the first-stage draw rollers.

10. A process according to any one of the preceding claims which comprises passing the filaments through a heated zone of a temperature 190—250° C. between the first-stage draw rollers and the second-stage draw rollers.

11. A process according to any one of the preceding claims wherein the filaments are composed of ethylene - 2,6 - naphthalate homopolymer.

12. A process according to any one of the preceding claims wherein the total draw ratio is at least 6.0X.

13. A process according to any one of the preceding claims wherein the undrawn filaments have been prepared by melt-spinning the ethylene - 2,6 - naphthalate polymer int an atmosphere whose temperature is controlled from the spinneret to the point where said atmospheric temperature becomes the secondary transition point of the polymer in such a way that

(1) when $0 < X \leqq X_1$
$$2X - 10 \leqq T - Ts \leqq 6X + 10$$

(2) when $X_1 < X \leqq X_2$
$$2X_1 - 10 \leqq T - Ts \leqq 6X_1 + 10$$

(3) when $X > X_2$
$$2X_1 - 6.4(X - X_2) - 10 \leqq T - Ts \leqq 6X_1 - 3.8(X - X_2) + 10$$

wherein T is the temperature of the atmosphere surrounding the yarn (°C.), Ts is the spinning temperature (°C.), X is the distance from the spinneret (cm), X_1, equals 7Q and X_2 equals 22Q, where Q is the flow rate through a single spinneret orifice (g/min).

14. A process according to any one of the preceding claims substantially as hereinbefore described with reference to and as illustrated in Figure 2 of the accompanying drawings.

15. A process according to any one of the preceding claims substantially as hereinbefore described with reference to and as illustrated in Figure 3 of the accompanying drawings.

16. Drawn filaments prepared by a process as claimed in any one of the preceding claims.

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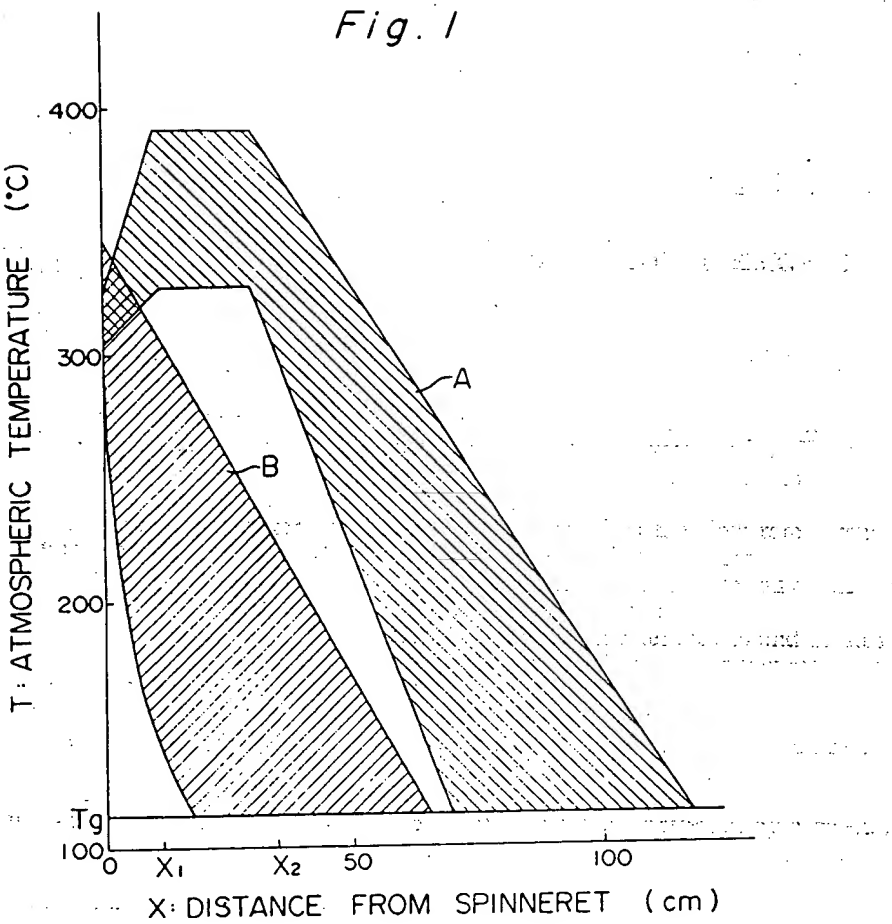
Sheet 1

Fig. 1



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Sheet 2

Fig. 2

Fig. 3